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(54) **Solventless or high solids-containing silicone pressure sensitive adhesive compositions.**

(57) Solventless and high solids-containing silicone pressure sensitive adhesive compositions having high peel adhesion and high tack are provided, comprising (A) a toluene-soluble resinous copolymer containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units ; (B) a vinyl-terminated polydiorganosiloxane ; (C) a hydrogen-terminated polydiorganosiloxane ; (D) a hydrosilation catalyst ; and (E) from 0 to about 10 percent by weight of an organic solvent ; provided that the combined viscosity of (B) and (C) is from about 10 to about 500 centipoises at 25°C., the combined crosslink densities of (B) and (C) is from about 0.3 to about 5.0 %; preferably 0.3 to about 2.0%, and the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) is in the range of from about 0.8 :1 to about 1.5 :1 and preferably about 1 :1.

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Cross Reference to Related Applications

Reference is made to the concurrently filed applications identified as Attorney Docket Nos. 60SI-1406 and 60SI-1449.

Background of the Invention

The present invention relates to silicone compositions suitable for forming pressure sensitive adhesive compositions. More particularly, the present invention relates to solventless or high solids-containing, addition-curable silicone compositions suitable for forming pressure sensitive adhesive compositions having excellent tack and adhesive properties.

The term "pressure sensitive adhesive" (PSA) as used herein refers to adhesives that can be adhered to a surface and yet can be stripped from the surface without transferring more than trace quantities of adhesive to the surface, and can be readhered to the same or another surface because the adhesive retains some or all of its tack and adhesive strength.

Silicone pressure sensitive adhesives have excellent adhesive and cohesive strength and high tack as well as excellent heat resistance, cold resistance, electrical properties, and the like, which makes them applicable for use as electrical-insulating tape and for various pressure-sensitive products which must be resistant to hot and cold.

However, a drawback associated with silicone pressure sensitive adhesives is the use, handling, and emission of flammable and volatile organic compounds, e.g., organic solvents, in the preparation of the pressure sensitive adhesives from compositions containing high levels of organic solvent. Conventional pressure sensitive adhesives are made using high viscosity polymer inputs. Solvent is generally used for the purpose of reducing the viscosity of the composition to a level which renders the curable composition processable. It would be desirable to provide solventless or high solids containing (i.e., low solvent-containing) pressure sensitive adhesive silicone compositions containing low viscosity polymer inputs.

Another drawback associated with conventional pressure sensitive adhesives is their requirement for high cure temperature, e.g., 165°C and higher, in order to cure effectively. Because such pressure sensitive adhesives require high temperatures to cure, they cannot be used on substrates such as polyolefin-backed substrates which are sensitive to high temperatures.

Addition-curable, low solvent-containing silicone compositions capable of curing to form pressure sensitive adhesive compositons are known in the art.

U.S. Patent No. 3,983,298 (Hahn et al.) is directed to a silicone composition suitable for use as a pressure sensitive adhesive and obtained by mixing components consisting essentially of (a) 50-60 parts by weight of a solid, benzene-soluble resin copolymer consisting essentially of $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, which is known as an "MQ" resin, (b) 40-50 parts by weight of a vinyl-terminated polydiorgano-siloxane having a viscosity of from 20,000 to 100,000 centipoises at 25°C., (c) a hydrogen-containing organopolysiloxane in an amount sufficient to provide from 1.0 to 20.0 silicon-bonded hydrogen atoms for every olefinically unsaturated radical in the total of (a) plus (b), and (d) a platinum-containing catalyst. It is pointed out in Hahn et al. that compositions of the prior art based on mixtures of a benzene soluble resin copolymer containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units (hereinafter sometimes referred to as "MQ resin") and low viscosity silicones do not form pressure sensitive adhesive compositions.

U.S. Patent No. 4,774,297 (Murakami et al.) is directed to a composition suitable for forming a pressure sensitive adhesive having excellent tack and adhesive strength, comprising (A) 30-70 parts by weight of a vinyl-terminated polydiorganosiloxane having a viscosity of at least 500,000 centipoises at 25°C., (B) 70-30 parts by weight of an organopolysiloxane containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, (C) an organohydrogensiloxane in an amount sufficient to provide 1-20 silicon-bonded hydrogen atoms per alkenyl group, (D) a platinum-containing catalyst, and (E) from 25-400 parts by weight of an organic solvent. The vinyl polymer used in the Murakami et al. composition has a viscosity of at least 500,000 centipoises and preferably at least one million centipoises at 25°C.

European Patent Application No. 0269454 (Murakami et al.) discloses a composition suitable for forming a pressure sensitive adhesive having excellent tack and adhesive strength and comprising an alkenyl group-containing silicone polymer, a tackifying silicone resin, an organohydrogensiloxane, and a platinum-containing catalyst. There is said to be no specific restriction on the molecular weight of the alkenyl group-containing silicone polymer as long as no adverse effect accrues with respect to the workability of the pressure sensitive adhesive composition. If the pressure sensitive adhesive composition is solventless, the viscosity of the alkenyl group-containing silicone polymer is no more than 100,000 centipoises at 25°C, while in a solvent-containing composition, the alkenyl group-containing silicone polymer should have a viscosity of at least one million cen-

tipoises at 25°C. The organohydrogenpolysiloxane should be present in an amount sufficient to provide 1 to 40 silicon-bonded hydrogen atoms per alkenyl group in the composition. The Murakami et al. reference does not disclose a pressure sensitive adhesive composition prepared with low viscosity vinyl-functional silicones.

U.S. Patent No. 4,988,779 (Medford et al.) discloses a composition having a solvent content of no more than 5-10% by weight and suitable for forming a pressure sensitive adhesive, wherein the composition comprises from 30 to 50 parts of a vinyl endblocked polydiorganosiloxane fluid having a viscosity of from 500 to 10,000 centipoises at 25°C., from 50 to 70 parts of a benzene soluble resin copolymer containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, an organopolysiloxane having silicon bonded hydrogen atoms, and a platinum catalyst. The hydrogen-containing organopolysiloxane is present in an amount sufficient to provide from 1.0 to 30.0 silicon bonded hydrogen atoms for every olefinically unsaturated radical in the composition.

European Patent Application No. 0355991 (Boardman) is directed to a pressure sensitive adhesive composition having a high solids content, i.e., typically in excess of 95% by weight, preferably in excess of 98% by weight, comprising (a) an MQ resin containing silicon-bonded hydroxyl radicals ranging from 1 to 4 percent by weight of the copolymer, (b) an alkenyl-terminated polydiorganosiloxane, (c) a hydrogen-terminated polydiorganosiloxane, (d) a crosslinking agent, and (e) a hydrosilation catalyst. The number of repeating units in the alkenyl-terminated polydiorganosiloxane and the hydrogen-terminated polydiorganosiloxane ranges from 0 to 1000 in each. The crosslinking agent is an organosiloxane containing more than two groups that will condense with a hydrogen or alkenyl group of an organopolysiloxane in a hydrosilation reaction. The ratio of the total number of silicon-bonded alkenyl groups present in (d) and (b) to the total number of silicon-bonded hydrogen atoms present in (d) and (c) ranges from 0.8 to 1.2, i.e., the ratio of the total number of silicon-bonded hydrogen atoms in (d) and (c) to the total number of silicon-bonded alkenyl groups in (d) and (b) ranges from 0.83-1.25:1. The results reported in the examples show that the tack obtained therein ranged from low to moderate. The Boardman composition contains an external crosslinking agent, the examples therein using 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane as the crosslinker. It is desirable to provide a solventless or high solids-containing addition-curable pressure sensitive adhesive composition which does not require the presence of an external crosslinker.

It is further desirable to provide solventless or high solids-containing pressure sensitive adhesive compositions containing polymer inputs having viscosities lower than those taught in the prior art. It is also desirable to provide solventless or high solids containing pressure sensitive adhesive compositions which cure to form pressure sensitive adhesives having high tack values as well as high peel adhesion values. It is further desirable to provide solventless or high solids content, addition-curable silicone pressure sensitive adhesive compositions which can be cured effectively at relatively low temperatures to form pressure sensitive adhesives having high tack and peel adhesion values.

Such silicone pressure sensitive adhesive compositions are provided by the present invention.

Summary of the Invention

The present invention is directed to a solventless or low solvent-containing organopolysiloxane composition curable to produce a pressure sensitive adhesive having high tack and high peel adhesion properties, comprising by weight:

(A) from about 50 to about 75 parts by weight of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to about 6 carbon atoms, the resinous copolymer comprising from about 0.2% to about 5.0% by weight, based on the total weight of the copolymer, of hydroxy radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from about 0.6 to about 0.9 inclusive;

(B) an alkenyl-terminated polydiorganosiloxane having the general formula

$$\text{(I)} \qquad R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$$

wherein each R^1 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 1 to about 10 carbon atoms, "m" and "n" are numbers such that the sum of "m"+"n" is equal to a number in the range of from about 1 to about 300;

(C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

$$\text{(II)} \qquad R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$$

wherein each R^3 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, "a" and "b" each are numbers such that the sum of "a"+"b"is a number in the range of from 1 to about 300, there being greater than two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from about 25 to about 50 parts

by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from about 0.8:1 to about 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from about 0.3 to about 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from about 10 to about 500 centipoises at 25°C;

(D) a catalytic amount of a hydrosilation catalyst; and

(E) from 0 to about 10% by weight of an organic solvent.

The compositions of the present invention cure at a relatively low temperature, i.e., from about 120°C to about 140°C, to form pressure sensitive adhesives having a tack of greater than 200 grams/cm^2, preferably greater than 700 grams/cm^2; a peel adhesion strength greater than 20 ounces/inch, preferably greater than 25 ounce/inch. Furthermore, the compositions of this invention require no solvent to improve workability in the uncured state.

Detailed Description of the Invention

The term "crosslink density" as used herein refers to the value obtained by dividing the total number of moles of internal silicon-bonded hydrogen groups in (C) and/or internal silicon-bonded alkenyl groups in (D) by the total number of moles of internal silicon atoms in (C) and (D). The term "internal" refers to those groups bonded to non-terminal silicon atoms in the silicone chain. The "internal silicon atoms" are the non-terminal silicon atoms. As will be discussed in greater detail below, the crosslink density of the curable composition of this invention is critical to obtaining the superior peel adhesion and tack properties of the final pressure sensitive adhesive prepared from the low viscosity polymer inputs used in the present invention.

Component (A) of the composition of the present invention is a toluene-soluble, resinous organopolysiloxane copolymer which imparts tack to the cured pressure sensitive adhesive prepared from the composition. The resinous copolymer (A) comprises $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical containing from 1 to about 6 carbon atoms. At least 95% of all R groups are alkyl groups, preferably methyl. The total number of R radicals that have olefinic unsaturation is no more than 0.5%, and preferably is zero %, of all R radicals. The molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units is from about 0.6 to about 0.9 inclusive. The resinous copolymer comprises from about 0.2% to about 5.0% and preferably from about 1.0% to about 3.0%, by weight based on the total weight of the copolymer, of hydroxyl radicals.

Component (A) is present in the composition of this invention in an amount ranging from about 50 to about 75, preferably from about 50 to about 70, and most preferably from about 55 to about 62, parts by weight.

Methods for making the resinous copolymer (A) are known in the art. Reference is made, for example, to U.S. Patent No. 2,676, 182 to Daudt et al., which is hereby incorporated by reference herein. In the Daudt et al. method, a silica hydrosol is reacted under acidic conditions with a source of triorganosiloxy units such as a hexaorganodisiloxane, e.g., hexamethyldisiloxane, or a hydrolyzable triorganosilane, e.g., trimethylchlorosilane, or mixtures thereof, and recovering a benzene soluble resin copolymer having M and Q units.

The resinous copolymer (A) is a solid, resinous material and is most often available as a solution in a solvent such as xylene or toluene, generally as a 40% to 60% by weight solution. For ease of handling of the composition of the present invention, one part of the solution of the resinous copolymer is usually dissolved in some or all of the vinyl chain-stopped polysiloxane (B) and the other part of the solution of the resinous copolymer is usually dissolved in some or all of the hydride chain-stopped polysiloxane (C) and the solvent stripped from each of the resulting solutions to produce solutions of resinous copolymer (A) in the vinyl-chainstopped polysiloxane (B) and in the hydride-chainstopped polysiloxane (C). The solution of (A) and (B) typically contains from about 50 to about 75, preferably from about 50 to about 70, and most preferably from about 55 to about 62, parts by weight, of (A), and from about 25 to about 50, preferably from about 30 to about 50, and most preferably from about 38 to about 45 parts by weight, of (B). The solution of (A) and (C) typically contains from about 50 to about 75, preferably from about 50 to about 70, and most preferably from about 55 to about 62, parts by weigh, of (A), and from about 25 to about 50, preferably from about 30 to about 50, and most preferably from about 38 to about 45 parts by weight, of (C).

Component (B) of the composition of the present invention is an alkenyl-terminated polydiorganosiloxane having the general formula

$$\text{(I)} \qquad R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$$

wherein each R^1 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 1 to about 10 carbon atoms, "m" and "n" are each numbers such that the sum of "m"+"n" is equal to a number in the range of from about 1 to about 300.

In formula (I), R^1 is an alkyl group such as methyl, ethyl, and propyl, or an aryl group such as phenyl. Preferably, at least 99.5 percent and most preferably 100 percent of all R^1 radicals are alkyl and most preferably

methyl. R^2 is an alkenyl group such as vinyl, allyl, or propenyl. Preferably, R^2 is vinyl. The polysiloxane (B) must be terminated with silicon-bonded alkenyl groups so that polymer chain extension with the terminal hydride groups on (C) will occur during cure.

In formula (I) above, the sum of "m"+"n" is preferably a number ranging from about 10 to about 100, and most preferably from about 15 to about 25.

Alkenyl-terminated polydiorganosiloxanes (B) can be prepared by any of the conventional methods for preparing triorganosiloxane-terminated polydiorganosiloxanes. For example, a proper ratio of the appropriate hydrolyzable silanes, e.g., vinyldimethylchlorosilane and dimethyldichlorosilane, may be cohydrolyzed and condensed or alternately an appropriate 1,3-divinyltetraorganodisiloxane, e.g., symmetrical divinyldimethyldiphenyldisiloxane or divinyltetramethyldisiloxane, which furnishes the endgroups of the polydiorganosiloxane, may be equilibrated with an appropriate diorganopolysiloxane, e.g., octamethylcyclotetrasiloxane, in the presence of an acidic or basic catalyst. Regardless of the method of preparation of polydiorganosiloxane (B), there is usually coproduced a varying quantity of volatile, cyclic polydiorganosiloxanes. Volatile cyclic polydiorganosiloxanes, e.g., methyl tetramer, should be removed, since they are volatile and adversely affect pressure sensitive adhesive properties.

The amount used of polydiorganosiloxane (B), its formula (presented hereinabove as formula (I)), and its viscosity, for the purposes of this invention, refers to the essentially cyclic free portion of the polydiorganosiloxane. This essentially cyclic free portion can be determined by heating a sample of the polydiorganosiloxane at 150°C. for up to 1 hour to yield a residue. This residue will be essentially free of cyclic material with the exception of trace quantities of macrocyclic polydiorganosiloxanes which are non-volatile at 150°C. and atmospheric pressure.

Many of these polydiorganosiloxanes (B) are commercially available. Furthermore, component (B) can be homopolymers or copolymers or their several mixtures as long as they are alkenyl-endblocked polydiorganosiloxanes of formula (I).

Component (C) is an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

$$\text{(II)} \qquad R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$$

wherein each R^3 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, the sum of "a"+"b" being in the range of from 1 to about 300, there being greater than two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from about 25 to about 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from about 0.8:1 to about 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from about 0.3 to about 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from about 10 to about 300 centipoises at 25°C.

The term "compatible" means that the required amount of organohydrogenpolysiloxane (C) is at least partially soluble in the mixture of (A) and (B) and will exist in a uniformly dispersed state in the composition of this invention while participating in the curing reaction, until the cure has been effected.

Examples of alkyl groups represented by R^3 in formula (II) above include methyl, ethyl, and propyl. An example of an aryl group represented by R^3 is phenyl. Preferably, at least 99.5 percent and most preferably 100 percent of all R^3 radicals are alkyl and most preferably methyl.

The total amount of (B) and (C) is from about 25 to about 50, preferably from about 30 to about 50, and most preferably from about 38 to about 45, parts by weight.

The total crosslink density of (B) and (C) is from about 0.3 to about 5.0%, preferably from about 0.3 to about 2.0%, and most preferably from about 0.60 to about 1.2%. The internal silicon-bonded hydrogen groups in (C) and the silicon-bonded alkenyl groups in (B) function as crosslink sites and provide the necessary strength to the cured pressure sensitive adhesive.

The total crosslink density of (B) and (C) is critical to the present invention because if the crosslink density is too low, the cured pressure sensitive adhesive fails cohesively due to inadequate curing and leaves a residue on the substrate. If the crosslink density is too high, the cured pressure sensitive adhesive exhibits low tack and low adhesion peel values.

The molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) is in the range of from about 0.8:1 to about 1.5:1; preferably from about 0.9:1 to about 1.3:1, and most preferably about 1:1.

It is critical to the present invention that the molar ratio of silicon-bonded hydrogen groups (i.e., sometimes referred to herein as "SiH") in (C) to silicon-bonded alkenyl groups (i.e., sometimes referred to herein as "SiVi" or "SiVinyl") in (B) be in the ranges recited above. Maintaining an SiH:SiVi ratio within these limits ensures that a high molecular weight silicone network is formed during cure and ensures maximum tack values and thermal

stability of the cured pressure sensitive adhesive by eliminating residual SiH groups that can react with MQ resin, which cause the physical properties to change over time.

The amount of (C) sufficient to fulfill these ratio requirements is determined by measuring the alkenyl or vinyl contents of the desired types and amounts of components (A) and (B), which is typically done by ^{29}Silicone NMR. A precise amount of (C) can be used to provide a specific ratio of SiH to SiVinyl.

It is to be understood by those skilled in the art that the the SiH:SiVinyl molar ratio and crosslink density used in this invention are to be chosen such that the higher the SiH:SiVinyl molar ratio used, the higher the crosslink density used, and the lower the SiH:SiVinyl molar ratio used, the lower the crosslink density used. The proper combination of SiH:SiVinyl ratio and crosslink density can be determined by experimentation. It has been found that at a SiH:SiVinyl molar ratio of about 1:1, the crosslink density which should be used to obtain good pressure sensitive adhesive properties ranges from about 0.3 to about 2.0%, preferably from about 0.4 to about 1.5%, and most preferably 0.60 to about 1.2%.

The hydride polysiloxane (C) must be terminated with hydride groups so that polymer chain extension with the terminal vinyl groups on (B) will occur during cure.

The combined viscosity of (B) and (C) is from about 10 to about 500, preferably from about 10 to about 200, and most preferably from about 15 to about 25 , centipoises at 25°C. The combined viscosity of (B) and (C) must be 500 centipoises or less at 25°C because low viscosities are necessary to ensure that solventless mixtures of MQ resins with (B) and (C) are pourable.

Organohydrogenpolysiloxanes and their preparation are well known in the organosilicon polymer art; some are commercially available. Briefly, the preparation of organohydrogensiloxanes can be accomplished in any suitable manner such as by hydrolyzing silanes, such as chlorosilanes, and equilibrating the resulting hydrolyzate under acid catalysis. Alternately, a mixture of suitable siloxanes, such as cyclic siloxanes and linear siloxanes, can be copolymerized and equilibrated under acid catalysis. For example, a hydride-stopped silicone fluid suitable for use in the present invention can be prepared by reacting tetramethyldisiloxane with cyclic methyl tetramer of pre-determined ratio in the presence of Filtrol-20 as catalyst for 4-6 hours at 80-100°C. The Filtrol-20 catalyst is then removed by filtration and the residual reactants are removed by vacuum stripping.

Component (D) of the composition of the present invention is a catalyst which promotes the hydrosilation reaction. Useful catalysts for facilitating the hydrosilation curing reaction include precious metal catalysts such as those which use ruthenium, rhodium, palladium, osmium, iridium, and platinum, and complexes of these metals. Examples of suitable hydrosilation catalysts for use in the present invention are disclosed, for example, in U.S. Patent Nos. 3,159,601 and 3,159,662 (Ashby); 3,220,970 (Lamoreaux); 3,814,730 (Karstedt); 3,516,946 (Modic), and 4,029,629 (Jeram); all of the foregoing patents being hereby incorporated by reference herein.

Preferably, the hydrosilation catalyst used in the present invention is a platinum-containing catalyst. Suitable platinum-containing hydrosilation catalysts include any of the well known forms of platinum that are effective for catalyzing the reaction of silicon-bonded hydrogen atoms with silicon-bonded vinyl groups, such as finely divided metallic platinum, platinum on a finely divided carrier such as alumina, compounds of platinum such as chloroplatinic acid and complexes of platinum compounds.

Other suitable platinum-containing hydrosilation catalysts for use in the present invention include the platinum hydrocarbon complexes described in U.S. Patent Nos. 3,159,601 and 3,159,662 to Ashby, and the platinum alcoholate catalysts described in U.S. Patent No. 3,220,970 to Lamoreaux, as well as the platinum catalysts of U.S. Patent No. 3,814,730 to Karstedt. Additionally, the platinum chloride-olefin complexes described in U.S. Patent No. 3,516,946 to Modic are also useful herein. All of the aforesaid catalysts are thermally activated. A(so useful are the photoactive platinum catalysts such as those of U.S. Patent No. 4,510,094 to Drahnak. All of the U.S. Patents cited in the instant paragraph are incorporated by reference into the present disclosure.

Catalysts which are soluble in the mixture of (A), (B) and (C) are preferred, particularly if optical clarity is desired.

The platinum-containing catalyst (D) is present in the composition of this invention in an amount sufficient to provide at least 0.1 part by weight platinum for one million parts by weight of the combined weight of (A), (B), and (C). Frequently, such small amounts of catalyst are poisoned by trace amounts of impurities in the composition so it is advantageous to use the platinum catalyst in such quantities to provide at least 1.0 part per million (ppm). The amount of platinum-containing catalyst is not critical with respect to the upper limit but its cost would suggest that excessive quantites be avoided. Amounts of up to 200 ppm platinum are not unusual but preferably from 1 to 35 parts by weight of platinum for every one million parts by weight of the total of (A), (B), and (C) used.

The compositions of the present invention can further comprise up to about 10 percent by weight of an organic solvent. Suitable organic solvents include any of the solvents conventionally used with organosiloxanes and having a boiling point below approximately 250°C., such as aromatic hydrocarbons, e.g., benzene, toluene,

and xylene; aliphatic hydrocarbons such as hexane, heptane, and cyclohexane; halogenated hydrocarbon solvents such as trichloroethane and chloroform; naphthas such as petroleum ether, VM and P Naphtha and refined naphthas such as Naphthalite 66/3 and oxygenated solvents such as hydrocarbon ethers, e.g., tetrahydrofuran and the dimethylether of ethylene glycol; ketones such as methyl isobutyl ketone and esters such as ethyl acetate and the like. Mixtures of organic solvents can also be used.

The components of the compositions of this invention can be mixed in any manner such as in bulk or in organic solvent. Since the resinous copolymer (A) is a solid and is conveniently prepared and handled in an organic solvent, the preparation of the composition of this invention preferably uses an organic solvent, at least for the mixing of (A) and (B). The organic solvent can be any of the solvents recited above in connection with component (E). The mixing of the components can be accomplished by any of the techniques known in the art, such as milling, blending, stirring, and the like, either in batch or in continuous process.

The composition of this invention can be prepared, with or without the aid of solvent, by simply mixing (A), (B), (C), and (D) together in the stated proportions. The order of mixing of the components is not critical, except that the organopolysiloxane (C) and the catalyst (D) are preferably brought together last. If heat is used in the preparation of the compositions of this invention, it is preferred to add the organopolysiloxane (C) after all heating operations in the preparation process have been completed. The preceding system is referred to herein as a one-component system. However, the best method of preparing the composition of this invention is based on a two-component system, wherein two blends are used, one comprising the resinous copolymer (A), which may be dissolved in about an equal weight of an organic solvent to facilitate mixing, with polydiorganosiloxane (B) and the other blend comprising the resinous copolymer, which also may be dissolved in about an equal weight of an organic solvent to facilitate mixing, with polydiorganosiloxane (C), so as to form pre-made intermediates. This method is preferred because it faciliates control of the SiH/SiVinyl ratio. To obtain compositions having at least 90% and preferably about 100% solids, the copolymer /polydiorganosiloxane blends should be devolatilized under conditions equivalent to heating for 1 hour at 150°C at atmospheric pressure in order to obtain optimum pressure sensitive adhesive properties. Obviously, excessively high temperatures should be avoided when components (A) and (B) or their mixtures are being devolatilized. A temperature of 100°C., and preferably 80°C., should not be exceeded. The mixture of (A), (B) and solvent is devolatilized in thin film at 70°C at full vacuum. Additional solvent may be added to the cooled, devolatilized mixtures to obtain a desired viscosity. Catalyst (D) is added to the devolatilized mixture of (A) and (B) to complete the composition of the first component of the two-component system. The second mixture is prepared by blending (A), (C), and solvent and then devolatilizing the blend under vacuum at a temperature of 70°C. A small amount of addition-cure inhibitor and additional solvent may also be added to the cooled, devolatilized mixture of (A) and (C) or (A) and (B) to obtain a desired viscosity. The final composition is completed by mixing the two components in appropriate amounts.

Thus, in a preferred embodiment of the composition of the present invention, the composition comprises by weight:

(1) a solventless mixture comprising by weight from about 55 to about 62 parts by weight of (A) and from about 38 to about 45 parts by weight of (B);

(2) a solventless mixture comprising by weight from about 55 to about 62 parts by weight of (A) and from about 38 to about 45 parts by weight of (C); and

(3) a hydrosilation catalyst.

Small amounts of additional ingredients may be added to the composition of this invention if desired. For example, antioxidants, pigments, stabilizers, fillers, and the like, may be added as long as they do not materially reduce the pressure sensitive adhesive properties of these compositions. Volatile additives are preferably added after any solvent removal operations have been completed.

A long or longer "shelf life" can be obtained by mixing a platinum catalyst inhibitor in either of the two components of a two-component system or in the curable mixture in the case of a one component system. Platinum catalyst inhibitors which are useful in the composition of this invention and which display varying lengths of cure time inhibition in our compositions are those described in U.S. Patent Nos. 3,188,299; 3,188,300; 3,192,181; 3,344,111; 3,383,356; 3,445,420; 3,453,233; 3,453,234; and 3,532,649, and others which might be known in the art. All of the patents cited in the instant paragraph are incorporated by reference herein. Concrete examples of inhibitors which can be used in the composition of the present invention include the ene-ynes, such as 3-methyl-3-pentene-1-yne and 3,5-dimethyl-3-hexene-1-yne; the alkynyl alcohols, such as 3-methyl-1-butyne-3-ol; 3,5-dimethyl-1-hexyne-3-ol; 3-methyl-1-pentyne-3-ol; and phenylbutynol; the unsaturated ester, such as alkyl and substituted alkyl maleates; and polymethylvinylcyclosiloxanes.

The effectiveness of a platinum catalyst inhibitor depends on many factors such as its chemical composition, its physical properties, its concentration, and the like. For the purposes of this invention, an effective amount of any particular platinum catalyst inhibitor can be determined by routine experimentation. Since many

platinum catalyst inhibitors are relatively volatile it is preferable to add them to the compositions of this invention after any heating and/or vacuum operations of the preparative process have been completed. For maximum effectiveness, however, a platinum catalyst inhibitor should be added to the composition of this invention at least simultaneously with, and preferably prior to the mixing of components (C) and (D) or parts containing them.

The compositions of this invention, when containing a platinum catalyst inhibitor, can be cured by removing the inhibitor, for example, by evaporation at room temperature or higher or by deactivating the inhibitor by heating at a high temperature, e.g., 100°C. Curing is accomplished by heating the composition to a temperature of from 120°C. to 140°C., preferably about 130°C. Curing time is dependent on the SiH/SiVinyl molar ratio, the thickness of the pressure sensitive adhesive, and the catalyst and inhibitor levels. Generally, at temperatures of 120°C-140°C, a SiH/SiVinyl molar ratio of about 1.0:1, a PSA thickness of 1-4 mils, a platinum level of 25 ppm and an inhibitor level of 0.75% by weight of dimethylmaleate inhibitor, cure time is about 2 minutes. The exceptional pressure sensitive adhesive characteristics of these compositions are developed when the composition is cured and the cured composition is essentially free of organic solvent.

Preferably, the uncured composition of this invention should be used within a few hours after being prepared, although this time interval from preparation to use, otherwise known as "shelf life", can be extended to several days by cooling the mixture to a temperature of -20°C. or below. Equally long or longer "shelf life" can be realized by mixing a platinum catalyst inhibitor such as any of those described previously herein in either or both of the components of a two-component system is used or in the curable mixture in the case of a one-component system.

The uncured composition of this invention can be used as a solution in one or more of the organic solvents described above or the composition can be used with no solvent present. While it is possible to use as much as 10 percent and more of an organic solvent, typically no more than 1 percent, and frequently as little as about 0 percent by weight, based on the total weight of the composition, of one or more of the organic solvents described above is used to aid in the application of the composition. This can be accomplished simply by not removing all of the solvent that is used in the preparation of the composition. Alternately, all of the solvent that is used in the preparation of the composition can be removed and the desired amount of the same or another solvent can be added. If, during the preparation of the composition of this invention, any portion of the solvent is removed, particularly if heat and/or vacuum is used to remove the solvent, it is preferred to remove the solvent prior to the addition of other volatile components such as inhibitors or additives. Me removal of solvent can be accomplished by any of the known techniques such as entrainment in a stream of inert gas, evaporation, distillation, thin film stripping, and the like, and at any combination of temperature and pressure where the temperature is not allowed to exceed approximately 200°C., preferably about 150°C.

The compositions of this invention are useful as pressure sensitive adhesives and will readily stick to a solid support, whether flexible or rigid. The composition is simply applied to the surface of the support by any suitable coating means such as rolling, spreading, spraying, and the like; and cured as described above. It should be understood that the use of the compositions of this invention encompasses not only the application of the completed, uncured composition on the surface. For example, it is within the scope of this invention to apply a layer of a mixture of (A), (B), and (C) to a solid support and then add the hydrosilation catalyst (D), the needed mixing being accomplished by diffusion of (D) into the layer of (A), (B), and (C). It is preferred to delay the curing reaction until (D) is thoroughly diffused into the layer on the support. Any solvent that is present in the cured composition is preferably allowed to evaporate before the surface bearing the composition is adhered to a substrate, although this is not necessary.

The surface of the support and the substrate to which the support is adhered may be any known solid material such as metals, e.g., aluminum, silver, copper, iron, and their alloys; porous materials such as paper, wood, leather, and fabrics; organic polymeric materials such as polyolefins, e.g., polyethylene and polypropylene; fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride, silicone elastomers, silicone resins, polystyrene; polyamides, such as Nylon® polyamides, polyimides, polyesters, and acrylic polymers; painted surfaces; siliceous materials such as concrete, bricks, cinderblocks, and glass, e.g., glass cloth and the like. Porous materials such as glass cloth are often impregnated with a substance that will prevent the migration of the PSA from one surface to another surface of the support. It is also well known to chemically treat the surface of a fluorocarbon polymer support to enhance the adhesion of a PSA to said surface.

Solid supports bearing the cured compositions of this invention are reliably adhered to any solid substrate because the compositions possess the desirable combination of high tack and good adhesive strength.

Useful articles which can be prepared with the PSAs of this invention include pressure sensitive adhesive tapes, labels, emblems, and other decorative or informative signs, and the like. An especially useful article is one comprising a support, flexible or rigid, that can withstand extreme temperatures, hot and/or cold, and carrying on at least one surface thereof, the polyorganosiloxane PSAs of this invention. Such an article makes full use of the stability at high temperatures and the flexibility at low temperatures that the PSAs of this invention

possess.

A preferred article is a pressure sensitive adhesive tape comprising an impregnated glass cloth, a polyester polymer, a polyimide polymer, or a chemically treated fluorocarbon polymer support carrying on at least one surface thereof the cured compositions of this invention.

In order that those skilled in the art may better understand the present invention, the following examples are given to illustrate but not to limit the invention which is fully delineated by the appended claims.

Experimental

In the examples below, the term "MQ resin" refers to 60% by weight solution in toluene of a silicone resin containing $(CH_3)_3SiO_{1/2}$ ("M") units, and $SiO_{4/2}$ ("Q") units and having a silanol content of about 1 to 3 % by weight. The term "D_4" refers to octamethylcyclotetrasiloxane and "D_4^{Vi}" refers to 1,3,5,7-tetravinyl-tetramethylcyclotetrasiloxane. The platinum catalyst used in Examples 8-14 is the Karstedt catalyst, i.e., a solution of 5.2% platinum metal in xylene and 1,3-divinyltetramethyldisiloxane, which is disclosed in U.S. Patent No. 3,814,730.

Examples 1-7 Preparation of Intermediates

Seven vinyl-containing silicone fluids were synthesized having the general formula

$$Vi(CH_3)_2Si[OSi(CH_3)_2]_x(OSiCH_3Vi)_yOSi(CH_3)_2Vi$$

wherein Vi represents vinyl, and x, y, and the molecular weight in grams/mole are summarized in Table 1 below.

TABLE 1

Example No.	x	y	Molecular Weight (g/mol)
1	23.5	0.13	1940
2	21.5	0.28	1800
3	19.4	0.53	1670
4	20.0	1.42	1790
5	17.0	2.3	1650
6	10.1	9.5	1750
7	0	18.2	1790

The viscosities of the fluids prepared in Examples 1-7 were measured to be in the range of abourt 15-25 centipoises at 25°C.

The fluids used in Examples 1-7 were prepared as follows.

A vinyl-containing fluid having the formula $Vi(CH_3)_2SiOSi(CH_3)_2Vi$ was reacted with appropriate molar equivalents of D_4 and D_4^{Vi} in the presence of 0.1 mole % triflic acid. After stirring the neat reaction for 6 days, MgO was added to neutralize the acid. The mixture was filtered and the volatiles were removed by vacuum distillation. The resulting vinyl-terminated silicone fluids were characterized by Brookfield viscosity measurements and ^{29}Si NMR to accurately determine molecular weight.

The silicone fluids prepared above were then individually mixed with MQ resin, and the toluene was stripped to provide solventless mixtures containing 60% MQ resin and 40% vinyl-containing silicone fluid ("SiVinyl fluid").

Solventless MQ resin/hydride-containing silicone fluid mixtures were also prepared. A hydride-containing silicone fluid ("SiH fluid") was prepared having the general formula

$$H(CH_3)_2Si[OSi(CH_3)_2]_{20.8}OSi(CH_3)_2H$$

The SiH fluid had a molecular weight of 1680 grams/mole and a viscosity of about 16 centipoises at 25°C.

The SiH fluid was prepared as follows.

A hydrogen-containing fluid having the formula $H(CH_3)_2SiOSi(CH_3)_2H$ was reacted with an appropriate number molar equivalents of D_4 in the presence of 0.1 mol% triflic acid. After stirring the neat reaction for 12

hours, MgO was added to neutralize the acid. The mixture was filtered and the volatiles were removed by vacuum distillation. The resulting hydride-terminated silicone fluid was characterized by Brookfield viscosity measurements and ^1H and ^{29}Si NMR to accurately determine molecular weight.

The SiH fluid prepared above was then mixed with MQ resin, and the toluene was stripped to provide a solventless mixture containing 60% MQ resin and 40% SiH fluid.

Examples 8-14 Preparation of Pressure Sensitive Adhesives

Examples 8-14 illustrate the preparation of seven solventless pressure sensitive adhesives using the MQ resin/SiVinyl fluid mixtures and the MQ/SiH fluid mixture prepared in Examples 1-7 above.

Platinum catalyst (10 ppm of platinum) and 0.75% by weight of dimethylmaleate were added to the uncured PSA compositions, the dimethylmaleate being added to inhibit hydrosilation reactions at room temperature.

Seven pressure sensitive adhesives were prepared by the simple mixing of measured portions of the solventless MQ resin/SiVinyl fluids and MQ resin/SiH fluid described above such that the SiH/SiVinyl molar ratio was 1:1. Thin films having a thickness of about 1.5-2.0 mils of the uncured pressure sensitive adhesives were applied to 1.0 mil thick polyethylene terephthalate (PET) film with the use of a doctor blade. The resulting pressure sensitive adhesive was cured by heating to 130°C for 8 minutes.

The tack of 1.5-2.0 mil thick films of the cured pressure sensitive adhesives on 1.0 mil thick PET were measured using a Polyken Probe Tack Tester, manufactured by testing Machine Incorporated, fitted with a 0.5 centimeter probe and operated at 1 cm/sec rate with a dwell time of 1 second. Peel adhesion was determined using an Instron (Model 4202) fitted with a 10 pound load cell. Laminates of 1.5-2.0 mil thick films of the cured pressure sensitive adhesive on 1 mil thick PET were applied to stainless steel test panels using a 1 pound roller and allowed to stand for 20 minutes, then pulled at 180°C at a rate of 12 inches per minute.

The crosslink densities, tack and peel adhesion properties of the cured pressure sensitive adhesives prepared in Examples 8-14 are shown in Table 2 below.

TABLE 2

Examples 8-14:Properties			
Example No.	Crosslink Density (%)	Tack (grams/cm²)	Peel Adhesion (ounces/inch)
8	0.28	840	cohesive failure
9	0.61	760	30
10	1.2	810	31
11	2.5	less than 300	12
12	3.6	less than 300	transferred to steel
13	6.8	less than 300	transferred to steel
14	8.0	less than 300	transferred to steel

The data shown in Table 2 above indicates that at SiH:SiVinyl molar ratios of 1:1, acceptable pressure sensitive adhesive properties are obtained at a crosslink density of between 0.3 and 2.0%. Higher crosslink densities for a 1:1 SiH:SiVinyl molar ratio result in dry adhesives (tack values of less than 300 grams/cm^2) which transfer to the steel test panel. Lower crosslink densities result in cohesive failure due to inadequate curing.

Examples 15-20

Six pressure sensitive adhesives having a solvent content of less than 0.5% were prepared by mixing the following solventless mixtures in the appropriate stochiometric ratios:
Part A:

60 weight % MQ resin
40 weight % $Vi(CH_3)_2Si[OSi(CH_3)_2]_{21.5}[OSiCH_3Vi]_{0.28}OSi(CH_3)_2Vi$

Part B:

60 weight % MQ resin
40 weight % $H(CH_3)_2Si[OSi(CH_3)_2]_{20.8}OSi(CH_3)_2H$

The combined crosslink density of the vinyl and hydride polymers above is about 0.67%. The combined viscosities of the vinyl and hydride polymers in these examples is from about 15 to about 20 centipoise at 25°C.

Pressure sensitive adhesives were prepared from these mixtures with Karstedt's catalyst containing 25 ppm of platinum metal and 0.75% dimethylmaleate as inhibitor. The compositions were cured on PET substrates for 3 minutes at 130°C. The tack and peel adhesion properties of the cured compositions were measured as a function of SiH/SiVinyl ratio according to the procedures described earlier herein and are presented in Table 3 below.

TABLE 3

Examples 15-20:Properties				
Example No.	SiH/SiVinyl Ratio	Tack (g/cm^2)	Peel Adhesion (oz/in)	Crosslink Density (%)
15	0.9:1	730	24	0.7
16	1.0:1	760	30	0.66
17	1.05:1	940	27	0.65
18	1.1:1	960	26	0.63
19	1.2:1	820	22	0.60
20	1.3:1	870	24	0.57

Examples 15-20 illustrate that good peel adhesion properties are obtained when the SiH/SiVinyl ratio is from 0.9 to 1.3, particularly at 1:1. Examples 15-20 further illustrate that the higher the SiH/SiVinyl ratio, the lower the crosslink density needed to achieve good pressure sensitive adhesive properties.

Claims

1. An organopolysiloxane composition curable to produce a pressure sensitive adhesive having high tack and high peel adhesion, comprising by weight:

   (A) from about 50 to about 75 parts by weigh of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to about 6 carbon atoms, the resinous copolymer comprising from about 0.2% to about 5.0% by weight, based on the total weight of the copolymer, of hydroxyl radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from about 0.6 to about 0.9 inclusive;

   (B) an alkenyl-terminated polydiorganosiloxane having the general formula

   $$\text{(I)} \qquad R^2R^1{}_2SiO(R^1{}_2SiO)_m(R^2R^1SiO)_nSiR^1{}_2R^2$$

   wherein each R^1 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 1 to about 10 carbon atoms, "m" and "n" are numbers such that the sum of "m"+"n" is equal to a number in the range of from about 1 to about 300;

   (C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

   $$\text{(II)} \qquad R^3{}_2HSiO(R^3HSiO)_a(R^3{}_2SiO)_bSiHR^3{}_2$$

   wherein each R^3 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl

group, "a" and "b" each are numbers such that the sum of "a"+"b" is a number in the range of from 1 to about 300, there being greater than two silicon-bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from about 25 to about 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from about 0.8:1 to about 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from about 0.3 to about 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from about 10 to about 500 centipoises at 25°C;
(D) a catalytic amount of a hydrosilation catalyst; and
(E) from 0 to about 10% by weight of an organic solvent.

2. A composition according to claim 1 wherein the combined crosslink density of (B) and (C) is from about 0.3 to about 2.0% and the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) is about 1:1.

3. A composition according to claim 1 wherein the hydrosilation catalyst is a platinum-containing hydrosilation catalyst.

4. A composition according to claim 1 wherein the platinum-containing hydrosilation catalyst is present in an amount of at least 1.0 part by weight per 1 million parts of the total of (A), (B), and (C).

5. A composition according to claim 1 further comprising an inhibitor for the hydrosilation catalyst.

6. A composition according to claim 1 wherein R, R^1, and R^3 are each methyl.

7. A composition according to claim 1 wherein R^2 is a vinyl group.

8. A pressure sensitive adhesive tape comprising a flexible support carrying on at least one surface thereof the curable composition of claim 1.

9. A pressure sensitive adhesive tape according to claim 8 wherein the flexible support is an impregnated glass cloth, a polyester polymer, a polyimide polymer, or a chemically treated fluorocarbon polymer support.

10. A solventless organopolysiloxane composition curable to produce a pressure sensitive adhesive having high tack and high peel adhesion, comprising by weight:
(A) from about 50 to about 75 parts by weight of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to about 6 carbon atoms, the resinous copolymer comprising from about 0.2% to about 5.0% by weight, based on the total weight of the copolymer, of hydroxyl radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from about 0.6 to about 0.9 inclusive;
(B) an alkenyl-terminated polydiorganosiloxane having the general formula

$$\text{(I)} \qquad R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1\,SiO)_nSiR^1_2R^2$$

wherein each R^1 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 1 to about 10 carbon atoms, "m" and "n" are numbers such that the sum of "m"+"n" is equal to a number in the range of from about 1 to about 300;
(C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

$$\text{(II)} \qquad R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$$

wherein each R^3 is independently an alkyl group having from 1 to about 10 carbon atoms or an aryl group, "a" and "b" each are numbers such that the sum of "a"+"b" is a number in the range of from 1 to about 300, there being greater than two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from about 25 to about 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from about 0.8:1 to about 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from about 0.3 to about 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from about 10 to about 500 centipoises at 25°C; and
(D) a catalytic amount of a hydrosilation catalyst.

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Description

Background of the Invention

The present invention relates to silicone compositions suitable for forming pressure sensitive adhesive compositions. More particularly, the present invention relates to solventless or high solids-containing, addition-curable silicone compositions suitable for forming pressure sensitive adhesive compositions having excellent tack and adhesive properties.

The term "pressure sensitive adhesive" (PSA) as used herein refers to adhesives that can be adhered to a surface and yet can be stripped from the surface without transferring more than trace quantities of adhesive to the surface, and can be readhered to the same or another surface because the adhesive retains some or all of its tack and adhesive strength.

Silicone pressure sensitive adhesives have excellent adhesive and cohesive strength and high tack as well as excellent heat resistance, cold resistance, electrical properties, and the like, which makes them applicable for use as electrical-insulating tape and for various pressure-sensitive products which must be resistant to hot and cold.

However, a drawback associated with silicone pressure sensitive adhesives is the use, handling, and emission of flammable and volatile organic compounds, e.g., organic solvents, in the preparation of the pressure sensitive adhesives from compositions containing high levels of organic solvent. Conventional pressure sensitive adhesives are made using high viscosity polymer inputs. Solvent is generally used for the purpose of reducing the viscosity of the composition to a level which renders the curable composition processable. It would be desirable to provide solventless or high solids containing (i.e., low solvent-containing) pressure sensitive adhesive silicone compositions containing low viscosity polymer inputs.

Another drawback associated with conventional pressure sensitive adhesives is their requirement for high cure temperature, e.g., 165°C and higher, in order to cure effectively. Because such pressure sensitive adhesives require high temperatures to cure, they cannot be used on substrates such as polyolefin-backed substrates which are sensitive to high temperatures.

Addition-curable, low solvent-containing silicone compositions capable of curing to form pressure sensitive adhesive compositons are known in the art.

U.S. Patent No. 3,983,298 (Hahn et al.) is directed to a silicone composition suitable for use as a pressure sensitive adhesive and obtained by mixing components consisting essentially of (a) 50-60 parts by weight of a solid, benzene-soluble resin copolymer consisting essentially of $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, which is known as an "MQ" resin, (b) 40-50 parts by weight of a vinyl-terminated polydiorgano-siloxane having a viscosity of from 20,000 to 100,000 centipoises at 25°C., (c) a hydrogen-containing organopolysiloxane in an amount sufficient to provide from 1.0 to 20.0 silicon-bonded hydrogen atoms for every olefinically unsaturated radical in the total of (a) plus (b), and (d) a platinum-containing catalyst. It is pointed out in Hahn et al. that compositions of the prior art based on mixtures of a benzene soluble resin copolymer containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units (hereinafter sometimes referred to as "MQ resin") and low viscosity silicones do not form pressure sensitive adhesive compositions.

U.S. Patent No. 4,774,297 (Murakami et al.) is directed to a composition suitable for forming a pressure sensitive adhesive having excellent tack and adhesive strength, comprising (A) 30-70 parts by weight of a vinyl-terminated polydiorganosiloxane having a viscosity of at least 500,000 centipoises at 25°C., (B) 70-30 parts by weight of an organopolysiloxane containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, (C) an organohydrogensiloxane in an amount sufficient to provide 1-20 silicon-bonded hydrogen atoms per alkenyl group, (D) a platinum-containing catalyst, and (E) from 25-400 parts by weight of an organic solvent. The vinyl polymer used in the Murakami et al. composition has a viscosity of at least 500,000 centipoises and preferably at least one million centipoises at 25°C.

European Patent Application No. 0269454 (Murakami et al.) discloses a composition suitable for forming a pressure sensitive adhesive having excellent tack and adhesive strength and comprising an alkenyl group-containing silicone polymer, a tackifying silicone resin, an organohydrogensiloxane, and a platinum-containing catalyst. There is said to be no specific restriction on the molecular weight of the alkenyl group-containing silicone polymer as long as no adverse effect accrues with respect to the workability of the pressure sensitive adhesive composition. If the pressure sensitive adhesive composition is solventless, the viscosity of the alkenyl group-containing silicone polymer is no more than 100,000 centipoises at 25°C, while in a solvent-containing composition, the alkenyl group-containing silicone polymer should have a viscosity of at least one million centipoises at 25°C. The organohydrogenpolysiloxaneshould be present in an amount sufficient to provide 1 to 40 silicon-bonded hydrogen atoms per alkenyl group in the composition. The Murakami et al. reference does not disclose a pressure sensitive adhesive composition

prepared with low viscosity vinyl-functional silicones.

U.S. Patent No. 4,988,779 (Medford et al.) discloses a composition having a solvent content of no more than 5-10% by weight and suitable for forming a pressure sensitive adhesive, wherein the composition comprises from 30 to 50 parts of a vinyl endblocked polydiorganosiloxane fluid having a viscosity of from 500 to 10,000 centipoises at 25 °C., from 50 to 70 parts of a benzene soluble resin copolymer containing $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units, an organopolysiloxane having silicon bonded hydrogen atoms, and a platinum catalyst. The hydrogen-containing organopolysiloxane is present in an amount sufficient to provide from 1.0 to 30.0 silicon bonded hydrogen atoms for every olefinically unsaturated radical in the composition.

European Patent Application No. 0355991 (Boardman) is directed to a pressure sensitive adhesive composition having a high solids content, i.e., typically in excess of 95% by weight, preferably in excess of 98% by weight, comprising (a) an MQ resin containing silicon-bonded hydroxyl radicals ranging from 1 to 4 percent by weight of the copolymer, (b) an alkenyl-terminated polydiorganosiloxane, (c) a hydrogen-terminated polydiorganosiloxane, (d) a crosslinking agent, and (e) a hydrosilation catalyst. The number of repeating units in the alkenyl-terminated polydiorganosiloxane and the hydrogen-terminated polydiorganosiloxane ranges from 0 to 1000 in each. The crosslinking agent is an organosiloxane containing more than two groups that will condense with a hydrogen or alkenyl group of an organopolysiloxane in a hydrosilation reaction. The ratio of the total number of silicon-bonded alkenyl groups present in (d) and (b) to the total number of silicon-bonded hydrogen atoms present in (d) and (c) ranges from 0.8 to 1.2, i.e., the ratio of the total number of silicon-bonded hydrogen atoms in (d) and (c) to the total number of silicon-bonded alkenyl groups in (d) and (b) ranges from 0.83-1.25:1. The results reported in the examples show that the tack obtained therein ranged from low to moderate. The Boardman composition contains an external crosslinking agent, the examples therein using 1,3,5,7-tetravinyl-tetramethylcyclotetrasiloxane as the crosslinker. It is desirable to provide a solventless or high solids-containing addition-curable pressure sensitive adhesive composition which does not require the presence of an external crosslinker.

It is further desirable to provide solventless or high solids-containing pressure sensitive adhesive compositions containing polymer inputs having viscosities lower than those taught in the prior art. It is also desirable to provide solventless or high solids containing pressure sensitive adhesive compositions which cure to form pressure sensitive adhesives having high tack values as well as high peel adhesion values. It is further desirable to provide solventless or high solids content, addition-curable silicone pressure sensitive adhesive compositions which can be cured effectively at relatively low temperatures to form pressure sensitive adhesives having high tack and peel adhesion values.

Such silicone pressure sensitive adhesive compositions are provided by the present invention.

Summary of the Invention

The present invention is directed to a solventless or low solvent-containing organopolysiloxane composition curable to produce a pressure sensitive adhesive comprising by weight:

(A) from 50 to 75 parts by weight of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to about 6 carbon atoms, the resinous copolymer comprising from 0.2% to 5.0% by weight, based on the total weight of the copolymer, of hydroxyl radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from 0.6 to 0.9 inclusive;

(B) an alkenyl-terminated polydiorganosiloxane having the general formula

(I) $R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$

wherein each R^1 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 2 to 10 carbon atoms, "m" and "n" are numbers such that the sum of "m" + "n" is equal to a number in the range of from 1 to 300;

(C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

(II) $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$

wherein each R^3 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, "a" and "b" each are numbers such that the sum of "a" + "b" is a number in the range of from 1 to 300, there being at least two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing

more than one silicon bonded hydrogen atom; the total of (B) and (C) being from 25 to 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from 0.8:1 to 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from 0.3 to 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from 10 to 500 mPa.s (centipoises) at 25 °C;

(D) a catalytic amount of a hydrosilation catalyst; and

(E) from 0 to 10% by weight of an organic solvent.

The compositions of the present invention cure at a relatively low temperature, i.e., from 120 °C to 140 °C, to form pressure sensitive adhesives having a tack of greater than 200 grams/cm^2, preferably greater than 700 grams/cm^2; a peel adhesion strength greater than 22.3 g/mm (20 ounces/inch), preferably greater than 27.9 g/mm (25 ounces/inch). Furthermore, the compositions of this invention require no solvent to improve workability in the uncured state.

Detailed Description of the Invention

The term "crosslink density" as used herein refers to the value obtained by dividing the total number of moles of internal silicon-bonded hydrogen groups in (C) and/or internal silicon-bonded alkenyl groups in (B) by the total number of moles of internal silicon atoms in (C) and (B). The term "internal" refers to those groups bonded to non-terminal silicon atoms in the silicone chain. The "internal silicon atoms" are the non-terminal silicon atoms. As will be discussed in greater detail below, the crosslink density of the curable composition of this invention is critical to obtaining the superior peel adhesion and tack properties of the final pressure sensitive adhesive prepared from the low viscosity polymer inputs used in the present invention.

Component (A) of the composition of the present invention is a toluene-soluble, resinous organopolysiloxane copolymer which imparts tack to the cured pressure sensitive adhesive prepared from the composition. The resinous copolymer (A) comprises $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical containing from 1 to 6 carbon atoms. At least 95% of all R groups are alkyl groups, preferably methyl. The total number of R radicals that have olefinic unsaturation is no more than 0.5%, and preferably is zero %, of all R radicals. The molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units is from 0.6 to 0.9 inclusive. The resinous copolymer comprises from 0.2% to 5.0% and preferably from 1.0% to 3.0%, by weight based on the total weight of the copolymer, of hydroxyl radicals.

Component (A) is present in the composition of this invention in an amount ranging from 50 to 75, preferably from 50 to 70, and most preferably from 55 to 62, parts by weight.

Methods for making the resinous copolymer (A) are known in the art. Reference is made, for example, to U.S. Patent No. 2,676,182 to Daudt et al., which is hereby incorporated by reference herein. In the Daudt et al. method, a silica hydrosol is reacted under acidic conditions with a source of triorganosiloxy units such as a hexaorganodisiloxane, e.g., hexamethyldisiloxane, or a hydrolyzable triorganosilane, e.g., trimethylchlorosilane, or mixtures thereof, and recovering a benzene soluble resin copolymer having M and Q units.

The resinous copolymer (A) is a solid, resinous material and is most often available as a solution in a solvent such as xylene or toluene, generally as a 40% to 60% by weight solution. For ease of handling of the composition of the present invention, one part of the solution of the resinous copolymer is usually dissolved in some or all of the vinyl chain-stopped polysiloxane (B) and the other part of the solution of the resinous copolymer is usually dissolved in some or all of the hydride chain-stopped polysiloxane (C) and the solvent stripped from each of the resulting solutions to produce solutions of resinous copolymer (A) in the vinyl-chainstopped polysiloxane (B) and in the hydride-chainstopped polysiloxane (C). The solution of (A) and (B) typically contains from 50 to 75, preferably from 50 to 70, and most preferably from 55 to 62, parts by weight, of (A), and from 25 to 50, preferably from 30 to 50, and most preferably from 38 to 45 parts by weight, of (B). The solution of (A) and (C) typically contains from 50 to 75, preferably from 50 to 70, and most preferably from 55 to 62, parts by weight, of (A), and from 25 to 50, preferably from 30 to 50, and most preferably from 38 to 45 parts by weight, of (C).

Component (B) of the composition of the present invention is an alkenyl-terminated polydiorganosiloxane having the general formula

(I) $R^2R^1{}_2SiO(R^1{}_2SiO)_m(R^2R^1SiO)_nSiR^1{}_2R^2$

wherein each R^1 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 2 to 10 carbon atoms, "m" and "n" are each numbers such that the sum of "m" + "n" is equal to a number in the range of from 1 to 300.

In formula (I), R^1 is an alkyl group such as methyl, ethyl, and propyl, or an aryl group such as phenyl. Preferably, at least 99.5 percent and most preferably 100 percent of all R^1 radicals are alkyl and most preferably methyl. R^2 is an alkenyl group such as vinyl, allyl, or propenyl. Preferably, R^2 is vinyl. The polysiloxane (B) must be terminated with silicon-bonded alkenyl groups so that polymer chain extension with the terminal hydride groups on (C) will occur during cure.

In formula (I) above, the sum of "m" + "n" is preferably a number ranging from 10 to 100, and most preferably from 15 to 25.

Alkenyl-terminated polydiorganosiloxanes (B) can be prepared by any of the conventional methods for preparing triorganosiloxane-terminated polydiorganosiloxanes. For example, a proper ratio of the appropriate hydrolyzable silanes, e.g., vinyldimethylchlorosilane and dimethyldichlorosilane, may be cohydrolyzed and condensed or alternately an appropriate 1,3-divinyltetraorganodisiloxane, e.g., symmetrical divinyldimethyldiphenyldisiloxane or divinyltetramethyldisiloxane, which furnishes the endgroups of the polydiorganosiloxane, may be equilibrated with an appropriate diorganopolysiloxane, e.g., octamethylcyclotetrasiloxane, in the presence of an acidic or basic catalyst. Regardless of the method of preparation of polydiorganosiloxane (B), there is usually coproduced a varying quantity of volatile, cyclic polydiorganosiloxanes. Volatile cyclic polydiorganosiloxanes, e.g., methyl tetramer, should be removed, since they are volatile and adversely affect pressure sensitive adhesive properties.

The amount used of polydiorganosiloxane (B), its formula (presented hereinabove as formula (I)), and its viscosity, for the purposes of this invention, refers to the essentially cyclic free portion of the polydiorganosiloxane. This essentially cyclic free portion can be determined by heating a sample of the polydiorganosiloxane at 150 °C. for up to 1 hour to yield a residue. This residue will be essentially free of cyclic material with the exception of trace quantities of macrocyclic polydiorganosiloxanes which are non-volatile at 150 °C. and atmospheric pressure.

Many of these polydiorganosiloxanes (B) are commercially available. Furthermore, component (B) can be homopolymers or copolymers or their several mixtures as long as they are alkenyl-endblocked polydiorganosiloxanes of formula (I).

Component (C) is an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

(II) $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$

wherein each R^3 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, the sum of "a" + "b" being in the range of from 1 to 300, there being at least two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from 25 to 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from 0.8:1 to 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from 0.3 to 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from 10 to 500 mPa.s (centipoises) at 25 °C.

The term "compatible" means that the required amount of organohydrogenpolysiloxane (C) is at least partially soluble in the mixture of (A) and (B) and will exist in a uniformly dispersed state in the composition of this invention while participating in the curing reaction, until the cure has been effected.

Examples of alkyl groups represented by R^3 in formula (II) above include methyl, ethyl, and propyl. An example of an aryl group represented by R^3 is phenyl. Preferably, at least 99.5 percent and most preferably 100 percent of all R^3 radicals are alkyl and most preferably methyl.

The total amount of (B) and (C) is from 25 to 50, preferably from 30 to 50, and most preferably from 38 to 45, parts by weight.

The total crosslink density of (B) and (C) is from 0.3 to 5.0%, preferably from 0.3 to 2.0%, and most preferably from 0.60 to 1.2%. The internal silicon-bonded hydrogen groups in (C) and the silicon-bonded alkenyl groups in (B) function as crosslink sites and provide the necessary strength to the cured pressure sensitive adhesive.

The total crosslink density of (B) and (C) is critical to the present invention because if the crosslink density is too low, the cured pressure sensitive adhesive fails cohesively due to inadequate curing and leaves a residue on the substrate. If the crosslink density is too high, the cured pressure sensitive adhesive exhibits low tack and low adhesion peel values.

The molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) is in the range of from 0.8:1 to 1.5:1; preferably from 0.9:1 to 1.3:1, and most preferably 1:1.

It is critical to the present invention that the molar ratio of silicon-bonded hydrogen groups (i.e., sometimes referred to herein as "SiH") in (C) to silicon-bonded alkenyl groups (i.e., sometimes referred to herein as "SiVi" or "SiVinyl") in (B) be in the ranges recited above. Maintaining an SiH:SiVi ratio within these limits ensures that a high molecular weight silicone network is formed during cure and ensures maximum tack values and thermal stability of the cured pressure sensitive adhesive by eliminating residual SiH groups that can react with MQ resin, which cause the physical properties to change over time.

The amount of (C) sufficient to fulfill these ratio requirements is determined by measuring the alkenyl or vinyl contents of the desired types and amounts of components (A) and (B), which is typically done by ^{29}Silicone NMR. A precise amount of (C) can be used to provide a specific ratio of SiH to SiVinyl.

It is to be understood by those skilled in the art that the SiH:SiVinyl molar ratio and crosslink density used in this invention are to be chosen such that the higher the SiH:SiVinyl molar ratio used, the higher the crosslink density used, and the lower the SiH:SiVinyl molar ratio used, the lower the crosslink density used. The proper combination of SiH:SiVinyl ratio and crosslink density can be determined by experimentation. It has been found that at a SiH:SiVinyl molar ratio of about 1:1, the crosslink density which should be used to obtain good pressure sensitive adhesive properties ranges from 0.3 to 2.0%, preferably from 0.4 to 1.5%, and most preferably 0.60 to 1.2%.

The hydride polysiloxane (C) must be terminated with hydride groups so that polymer chain extension with the terminal vinyl groups on (B) will occur during cure.

The combined viscosity of (B) and (C) is from 10 to 500, preferably from 10 to 200, and most preferably from 15 to 25 mPa.s, (centipoises) at 25°C. The combined viscosity of (B) and (C) must be 500 mPa.s (centipoises) or less at 25°C because low viscosities are necessary to ensure that solventless mixtures of MQ resins with (B) and (C) are pourable.

Organohydrogenpolysiloxanes and their preparation are well known in the organosilicon polymer art; some are commercially available. Briefly, the preparation of organohydrogensiloxanes can be accomplished in any suitable manner such as by hydrolyzing silanes, such as chlorosilanes, and equilibrating the resulting hydrolyzate under acid catalysis. Alternately, a mixture of suitable siloxanes, such as cyclic siloxanes and linear siloxanes, can be copolymerized and equilibrated under acid catalysis. For example, a hydride-stopped silicone fluid suitable for use in the present invention can be prepared by reacting tetramethyldisiloxane with cyclic methyl tetramer of pre-determined ratio in the presence of Filtrol-20 as catalyst for 4-6 hours at 80-100°C. The Filtrol-20 catalyst is then removed by filtration and the residual reactants are removed by vacuum stripping.

Component (D) of the composition of the present invention is a catalyst which promotes the hydrosilation reaction. Useful catalysts for facilitating the hydrosilation curing reaction include precious metal catalysts such as those which use ruthenium, rhodium, palladium, osmium, iridium, and platinum, and complexes of these metals. Examples of suitable hydrosilation catalysts for use in the present invention are disclosed, for example, in U.S. Patent Nos. 3,159,601 and 3,159,662 (Ashby); 3,220,970 (Lamoreaux); 3,814,730 (Karstedt); 3,516,946 (Modic), and 4,029,629 (Jeram); all of the foregoing patents being hereby incorporated by reference herein.

Preferably, the hydrosilation catalyst used in the present invention is a Platinum-containing catalyst. Suitable platinum-containing hydrosilation catalysts include any of the well known forms of platinum that are effective for catalyzing the reaction of silicon-bonded hydrogen atoms with silicon-bonded vinyl groups, such as finely divided metallic platinum, platinum on a finely divided carrier such as alumina, compounds of platinum such as chloroplatinic acid and complexes of platinum compounds.

Other suitable platinum-containing hydrosilation catalysts for use in the present invention include the platinum hydrocarbon complexes described in U.S. Patent Nos. 3,159,601 and 3,159,662 to Ashby, and the platinum alcoholate catalysts described in U.S. Patent No. 3,220,970 to Lamoreaux, as well as the platinum catalysts of U.S. Patent No. 3,814,730 to Karstedt. Additionally, the platinum chloride-olefin complexes described in U.S. Patent No. 3,516,946 to Modic are also useful herein. All of the aforesaid catalysts are thermally activated. Also useful are the photoactive platinum catalysts such as those of U.S. Patent No. 4,510,094 to Drahnak. All of the U.S. Patents cited in the instant paragraph are incorporated by reference into the present disclosure.

Catalysts which are soluble in the mixture of (A), (B) and (C) are preferred, particularly if optical clarity is desired.

The platinum-containing catalyst (D) is present in the composition of this invention in an amount sufficient to provide at least 0.1 part by weight platinum for one million parts by weight of the combined weight of (A), (B), and (C). Frequently, such small amounts of catalyst are poisoned by trace amounts of impurities in the composition so it is advantageous to use the platinum catalyst in such quantities to provide at least 1.0 part per million (ppm). The amount of platinum-containing catalyst is not critical with respect to

the upper limit but its cost would suggest that excessive quantites be avoided. Amounts of up to 200 ppm platinum are not unusual but preferably from 1 to 35 parts by weight of platinum for every one million parts by weight of the total of (A), (B), and (C) used.

The compositions of the present invention can further comprise up to about 10 percent by weight of an organic solvent. Suitable organic solvents include any of the solvents conventionally used with organosiloxanes and having a boiling point below approximately 250 °C., such as aromatic hydrocarbons, e.g., benzene, toluene, and xylene; aliphatic hydrocarbons such as hexane, heptane, and cyclohexane; halogenated hydrocarbon solvents such as trichloroethane and chloroform; naphthas such as petroleum ether, VM and P Naphtha and refined naphthas such as Naphthalite 66/3 and oxygenated solvents such as hydrocarbon ethers, e.g., tetrahydrofuran and the dimethylether of ethylene glycol; ketones such as methyl isobutyl ketone and esters such as ethyl acetate and the like. Mixtures of organic solvents can also be used.

The components of the compositions of this invention can be mixed in any manner such as in bulk or in organic solvent. Since the resinous copolymer (A) is a solid and is conveniently prepared and handled in an organic solvent, the preparation of the composition of this invention preferably uses an organic solvent, at least for the mixing of (A) and (B). The organic solvent can be any of the solvents recited above in connection with component (E). The mixing of the components can be accomplished by any of the techniques known in the art, such as milling, blending, stirring, and the like, either in batch or in continuous process.

The composition of this invention can be prepared, with or without the aid of solvent, by simply mixing (A), (B), (C), and (D) together in the stated proportions. The order of mixing of the components is not critical, except that the organopolysiloxane (C) and the catalyst (D) are preferably brought together last. If heat is used in the preparation of the compositions of this invention, it is preferred to add the organopolysiloxane (C) after all heating operations in the preparation process have been completed. The preceding system is referred to herein as a one-component system. However, the best method of preparing the composition of this invention is based on a two-component system, wherein two blends are used, one comprising the resinous copolymer (A), which may be dissolved in about an equal weight of an organic solvent to facilitate mixing, with polydiorganosiloxane (B) and the other blend comprising the resinous copolymer, which also may be dissolved in about an equal weight of an organic solvent to facilitate mixing, with polydiorganosiloxane (C), so as to form pre-made intermediates. This method is preferred because it faciliates control of the SiH/SiVinyl ratio. To obtain compositions having at least 90% and preferably about 100% solids, the copolymer /polydiorganosiloxane blends should be devolatilized under conditions equivalent to heating for 1 hour at 150 °C at atmospheric pressure in order to obtain optimum pressure sensitive adhesive properties. Obviously, excessively high temperatures should be avoided when components (A) and (B) or their mixtures are being devolatilized. A temperature of 100 °C., and preferably 80 °C., should not be exceeded. The mixture of (A), (B) and solvent is devolatilized in thin film at 70 °C at full vacuum. Additional solvent may be added to the cooled, devolatilized mixtures to obtain a desired viscosity. Catalyst (D) is added to the devolatilized mixture of (A) and (B) to complete the composition of the first component of the two-component system. The second mixture is prepared by blending (A), (C), and solvent and then devolatilizing the blend under vacuum at a temperature of 70 °C. A small amount of addition-cure inhibitor and additional solvent may also be added to the cooled, devolatilized mixture of (A) and (C) or (A) and (B) to obtain a desired viscosity. The final composition is completed by mixing the two components in appropriate amounts.

Thus, in a preferred embodiment of the composition of the present invention, the composition comprises by weight:

(1) a solventless mixture comprising by weight from 55 to 62 parts by weight of (A) and from 38 to 45 parts by weight of (B);

(2) a solventless mixture comprising by weight from 55 to 62 parts by weight of (A) and from 38 to 45 parts by weight of (C); and

(3) a hydrosilation catalyst.

Small amounts of additional ingredients may be added to the composition of this invention if desired. For example, antioxidants, pigments, stabilizers, fillers, and the like, may be added as long as they do not materially reduce the pressure sensitive adhesive properties of these compositions. Volatile additives are preferably added after any solvent removal operations have been completed.

A long or longer "shelf life" can be obtained by mixing a platinum catalyst inhibitor in either of the two components of a two-component system or in the curable mixture in the case of a one component system. Platinum catalyst inhibitors which are useful in the composition of this invention and which display varying lengths of cure time inhibition in our compositions are those described in U.S. Patent Nos. 3,188,299; 3,188,300; 3,192,181; 3,344,111; 3,383,356; 3,445,420; 3,453,233; 3,453,234; and 3,532,649, and others

which might be known in the art. All of the patents cited in the instant paragraph are incorporated by reference herein. Concrete examples of inhibitors which can be used in the composition of the present invention include the ene-ynes, such as 3-methyl-3-pentene-1-yne and 3,5-dimethyl-3-hexene-1-yne; the alkynyl alcohols, such as 3-methyl-1-butyne-3-ol; 3,5-dimethyl-1-hexyne-3-ol; 3-methyl-1-pentyne-3-ol; and phenylbutynol; the unsaturated ester, such as alkyl and substituted alkyl maleates; and polymethylvinylcyclosiloxanes.

The effectiveness of a platinum catalyst inhibitor depends on many factors such as its chemical composition, its physical properties, its concentration, and the like. For the purposes of this invention, an effective amount of any particular platinum catalyst inhibitor can be determined by routine experimentation. Since many platinum catalyst inhibitors are relatively volatile it is preferable to add them to the compositions of this invention after any heating and/or vacuum operations of the preparative process have been completed. For maximum effectiveness, however, a platinum catalyst inhibitor should be added to the composition of this invention at least simultaneously with, and preferably prior to the mixing of components (C) and (D) or parts containing them.

The compositions of this invention, when containing a platinum catalyst inhibitor, can be cured by removing the inhibitor, for example, by evaporation at room temperature or higher or by deactivating the inhibitor by heating at a high temperature, e.g., 100 °C. Curing is accomplished by heating the composition to a temperature of from 120 °C. to 140 °C., preferably about 130 °C. Curing time is dependent on the SiH/SiVinyl molar ratio, the thickness of the pressure sensitive adhesive, and the catalyst and inhibitor levels. Generally, at temperatures of 120 °C-140 °C, a SiH/SiVinyl molar ratio of about 1.0:1, a PSA thickness of 25.4-101.6 μm (1-4 mils), a platinum level of 25 ppm and an inhibitor level of 0.75% by weight of dimethylmaleate inhibitor, cure time is about 2 minutes. The exceptional pressure sensitive adhesive characteristics of these compositions are developed when the composition is cured and the cured composition is essentially free of organic solvent.

Preferably, the uncured composition of this invention should be used within a few hours after being prepared, although this time interval from preparation to use, otherwise known as "shelf life", can be extended to several days by cooling the mixture to a temperature of -20 °C. or below. Equally long or longer "shelf life" can be realized by mixing a platinum catalyst inhibitor such as any of those described previously herein in either or both of the components of a two-component system is used or in the curable mixture in the case of a one-component system.

The uncured composition of this invention can be used as a solution in one or more of the organic solvents described above or the composition can be used with no solvent present. While it is possible to use as much as 10 percent and more of an organic solvent, typically no more than 1 percent, and frequently as little as about 0 percent by weight, based on the total weight of the composition, of one or more of the organic solvents described above is used to aid in the application of the composition. This can be accomplished simply by not removing all of the solvent that is used in the preparation of the composition. Alternately, all of the solvent that is used in the preparation of the composition can be removed and the desired amount of the same or another solvent can be added. If, during the preparation of the composition of this invention, any portion of the solvent is removed, particularly if heat and/or vacuum is used to remove the solvent, it is preferred to remove the solvent prior to the addition of other volatile components such as inhibitors or additives. The removal of solvent can be accomplished by any of the known techniques such as entrainment in a stream of inert gas, evaporation, distillation, thin film stripping, and the like, and at any combination of temperature and pressure where the temperature is not allowed to exceed approximately 200 °C., preferably about 150 °C.

The compositions of this invention are useful as pressure sensitive adhesives and will readily stick to a solid support, whether flexible or rigid. The composition is simply applied to the surface of the support by any suitable coating means such as rolling, spreading, spraying, and the like; and cured as described above. It should be understood that the use of the compositions of this invention encompasses not only the application of the completed, uncured composition on the surface. For example, it is within the scope of this invention to apply a layer of a mixture of (A), (B), and (C) to a solid support and then add the hydrosilation catalyst (D), the needed mixing being accomplished by diffusion of (D) into the layer of (A), (B), and (C). It is preferred to delay the curing reaction until (D) is thoroughly diffused into the layer on the support. Any solvent that is present in the cured composition is preferably allowed to evaporate before the surface bearing the composition is adhered to a substrate, although this is not necessary.

The surface of the support and the substrate to which the support is adhered may be any known solid material such as metals, e.g., aluminum, silver, copper, iron, and their alloys; porous materials such as paper, wood, leather, and fabrics; organic polymeric materials such as polyolefins, e.g., polyethylene and polypropylene; fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride, silicone

elastomers, silicone resins, polystyrene; polyamides, such as Nylon® polyamides, polyimides, polyesters, and acrylic polymers; painted surfaces; siliceous materials such as concrete, bricks, cinderblocks, and glass, e.g., glass cloth and the like. Porous materials such as glass cloth are often impregnated with a substance that will prevent the migration of the PSA from one surface to another surface of the support. It is also well known to chemically treat the surface of a fluorocarbon polymer support to enhance the adhesion of a PSA to said surface.

Solid supports bearing the cured compositions of this invention are reliably adhered to any solid substrate because the compositions possess the desirable combination of high tack and good adhesive strength.

Useful articles which can be prepared with the PSAs of this invention include pressure sensitive adhesive tapes, labels, emblems, and other decorative or informative signs, and the like. An especially useful article is one comprising a support, flexible or rigid, that can withstand extreme temperatures, hot and/or cold, and carrying on at least one surface thereof, the polyorganosiloxane PSAs of this invention. Such an article makes full use of the stability at high temperatures and the flexibility at low temperatures that the PSAs of this invention possess.

A preferred article is a pressure sensitive adhesive tape comprising an impregnated glass cloth, a polyester polymer, a polyimide polymer, or a chemically treated fluorocarbon polymer support carrying on at least one surface thereof the cured compositions of this invention.

In order that those skilled in the art may better understand the present invention, the following examples are given to illustrate but not to limit the invention which is fully delineated by the appended claims.

Experimental

In the examples below, the term "MQ resin" refers to 60% by weight solution in toluene of a silicone resin containing $(CH_3)_3SiO_{1/2}$ ("M") units, and $SiO_{4/2}$ ("Q") units and having a silanol content of about 1 to 3 % by weight. The term "D_4" refers to octamethylcyclotetrasiloxane and "D_4^{Vi}" refers to 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane. The platinum catalyst used in Examples 8-14 is the Karstedt catalyst, i.e., a solution of 5.2% platinum metal in xylene and 1,3-divinyltetramethyldisiloxane, which is disclosed in U.S. Patent No. 3,814,730.

Examples 1-7 Preparation of Intermediates

Seven vinyl-containing silicone fluids were synthesized having the general formula

$$Vi(CH_3)_2Si[OSi(CH_3)_2]_x(OSiCH_3Vi)_yOSi(CH_3)_2Vi$$

wherein Vi represents vinyl, and x, y, and the molecular weight in grams/mole are summarized in Table 1 below.

TABLE 1

Example No.	x	y	Molecular Weight (g/mol)
1	23.5	0.13	1940
2	21.5	0.28	1800
3	19.4	0.53	1670
4	20.0	1.42	1790
5	17.0	2.3	1650
6	10.1	9.5	1750
7	0	18.2	1790

The viscosities of the fluids prepared in Examples 1-7 were measured to be in the range of about 15-25 mPa.s (centipoises) at 25 °C.

The fluids used in Examples 1-7 were prepared as follows.

A vinyl-containing fluid having the formula $Vi(CH_3)_2SiOSi(CH_3)_2Vi$ was reacted with appropriate molar equivalents of D_4 and D_4^{Vi} in the presence of 0.1 mole % triflic acid. After stirring the neat reaction for 6 days, MgO was added to neutralize the acid. The mixture was filtered and the volatiles were removed by

vacuum distillation. The resulting vinyl-terminated silicone fluids were characterized by Brookfield viscosity measurements and ^{29}Si NMR to accurately determine molecular weight.

The silicone fluids prepared above were then individually mixed with MQ resin, and the toluene was stripped to provide solventless mixtures containing 60% MQ resin and 40% vinyl-containing silicone fluid ("SiVinyl fluid").

Solventless MQ resin/hydride-containing silicone fluid mixtures were also prepared. A hydride-containing silicone fluid ('SiH fluid") was prepared having the general formula

$$H(CH_3)_2Si[OSi(CH_3)_2]_{20.8}OSi(CH_3)_2H$$

The SiH fluid had a molecular weight of 1680 grams/mole and a viscosity of about 16 mPa.s (centipoises) at 25 °C.

The SiH fluid was prepared as follows.

A hydrogen-containing fluid having the formula $H(CH_3)_2SiOSi(CH_3)_2H$ was reacted with an appropriate number molar equivalents of D_4 in the presence of 0.1 mol% triflic acid. After stirring the neat reaction for 12 hours, MgO was added to neutralize the acid. The mixture was filtered and the volatiles were removed by vacuum distillation. The resulting hydride-terminated silicone fluid was characterized by Brookfield viscosity measurements and ^{1}H and ^{29}Si NMR to accurately determine molecular weight.

The SiH fluid prepared above was then mixed with MQ resin, and the toluene was stripped to provide a solventless mixture containing 60% MQ resin and 40% SiH fluid.

Examples 8-14 Preparation of Pressure Sensitive Adhesives

Examples 8-14 illustrate the preparation of seven solventless pressure sensitive adhesives using the MQ resin/SiVinyl fluid mixtures and the MQ/SiH fluid mixture prepared in Examples 1-7 above.

Platinum catalyst (10 ppm of platinum) and 0.75% by weight of dimethylmaleate were added to the uncured PSA compositions, the dimethylmaleate being added to inhibit hydrosilation reactions at room temperature.

Seven pressure sensitive adhesives were prepared by the simple mixing of measured portions of the solventless MQ resin/SiVinyl fluids and MQ resin/SiH fluid described above such that the SiH/SiVinyl molar ratio was 1:1. Thin films having a thickness of 38.1-50.8 µm (1.5-2.0 mils) of the uncured pressure sensitive adhesives were applied to 25.4 µm (1.0 mil) thick polyethylene terephthalate (PET) film with the use of a doctor blade. The resulting pressure sensitive adhesive was cured by heating to 130 °C for 8 minutes.

The tack of 38.1-50.4 µm (1.5-2.0 mil) thick films of the cured pressure sensitive adhesives on 25.4 µm (1.0 mil) thick PET were measured using a Polyken Probe Tack Tester, manufactured by testing Machine Incorporated, fitted with a 0.5 centimeter probe and operated at 1 cm/sec rate with a dwell time of 1 second. Peel adhesion was determined using an Instron (Model 4202) fitted with a 4.5 kg (10 pound) load cell. Laminates of 38.1-50.4 µm (1.5-2.0 mil) thick films of the cured pressure sensitive adhesive on 25.4 µm (1 mil thick) PET were applied to stainless steel test panels using a 4.5 kg (1 pound) roller and allowed to stand for 20 minutes, then pulled at 180 °C at a rate of 30.48 cm (12 inches) per minute.

The crosslink densities, tack and peel adhesion properties of the cured pressure sensitive adhesives prepared in Examples 8-14 are shown in Table 2 below.

TABLE 2

Examples 8-14: Properties			
Example No.	Crosslink Density (%)	Tack (grams/cm^2)	Peel Adhesion g/mm (ounces/inch)
8	0.28	840	cohesive failure
9	0.61	760	33.5 (30)
10	1.2	810	34.6 (31)
11	2.5	less than 300	13.4 (12)
12	3.6	less than 300	transferred to steel
13	6.8	less than 300	transferred to steel
14	8.0	less than 300	transferred to steel

The data shown in Table 2 above indicates that at SiH:SiVinyl molar ratios of 1:1, acceptable pressure sensitive adhesive properties are obtained at a crosslink density of between 0.3 and 2.0%. Higher crosslink densities for a 1:1 SiH:SiVinyl molar ratio result in dry adhesives (tack values of less than 300 grams/cm^2) which transfer to the steel test panel. Lower crosslink densities result in cohesive failure due to inadequate curing.

Examples 15-20

Six pressure sensitive adhesives having a solvent content of less than 0.5% were prepared by mixing the following solventless mixtures in the appropriate stochiometric ratios:

Part A:

60 weight % MQ resin

40 weight % $Vi(CH_3)_2Si[OSi(CH_3)_2]_{21.5}[OSiCH_3Vi]_{0.28}OSi(CH_3)_2Vi$

Part B:

60 weight % MQ resin

40 weight % $H(CH_3)_2Si[OSi(CH_3)_2]_{20.8}OSi(CH_3)_2H$

The combined crosslink density of the vinyl and hydride polymers above is about 0.67%. The combined viscosities of the vinyl and hydride polymers in these examples is from 15 to 20 mPa.s (centipoise) at 25 °C.

Pressure sensitive adhesives were prepared from these mixtures with Karstedt's catalyst containing 25 ppm of platinum metal and 0.75% dimethylmaleate as inhibitor. The compositions were cured on PET substrates for 3 minutes at 130 °C. The tack and peel adhesion properties of the cured compositions were measured as a function of SiH/SiVinyl ratio according to the procedures described earlier herein and are presented in Table 3 below.

TABLE 3

Examples 15-20: Properties				
Example No.	SiH/SiVinyl Ratio	Tack (g/cm^2)	Peel Adhesion g/mm (oz/in)	Crosslink Density (%)
15	0.9:1	730	26.8 (24)	0.7
16	1.0:1	760	33.5 (30)	0.66
17	1.05:1	940	30.1 (27)	0.65
18	1.1:1	960	29.0 (26)	0.63
19	1.2:1	820	24.6 (22)	0.60
20	1.3:1	870	26.8 (24)	0.57

Examples 15-20 illustrate that good peel adhesion properties are obtained when the SiH/SiVinyl ratio is from 0.9 to 1.3, particularly at 1:1. Examples 15-20 further illustrate that the higher the SiH/SiVinyl ratio, the lower the crosslink density needed to achieve good pressure sensitive adhesive properties.

Claims

1. An organopolysiloxane composition curable to produce a pressure sensitive adhesive comprising by weight:

(A) from 50 to 75 parts by weight of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to 6 carbon atoms, the resinous copolymer comprising from 0.2% to 5.0% by weight, based on the total weight of the copolymer, of hydroxyl radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from 0.6 to 0.9 inclusive;

(B) an alkenyl-terminated polydiorganosiloxane having the general formula

(I) $R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$

wherein each R^1 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 2 to 10 carbon atoms, "m" and "n" are numbers such that the

sum of "m" + "n" is equal to a number in the range of from 1 to 300;

(C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

(II) $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$

wherein each R^3 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, "a" and "b" each are numbers such that the sum of "a" + "b" is a number in the range of from 1 to 300, there being at least two silicon-bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from 25 to 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from 0.8:1 to 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from 0.3 to 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from 10 to 500 mPa.s (centipoises) at 25 °C;

(D) a catalytic amount of a hydrosilation catalyst; and

(E) from 0 to 10% by weight of an organic solvent.

2. A composition according to claim 1 wherein the combined crosslink density of (B) and (C) is from 0.3 to 2.0% and the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) is about 1:1.

3. A composition according to claim 1 wherein the hydrosilation catalyst is a platinum-containing hydrosilation catalyst.

4. A composition according to claim 1 wherein the platinum-containing hydrosilation catalyst is present in an amount of at least 1.0 part by weight per 1 million parts of the total of (A), (B), and (C).

5. A composition according to claim 1 further comprising an inhibitor for the hydrosilation catalyst.

6. A composition according to claim 1 wherein R, R^1, and R^3 are each methyl.

7. A composition according to claim 1 wherein R^2 is a vinyl group.

8. A pressure sensitive adhesive tape comprising a flexible support carrying on at least one surface thereof the curable composition of claim 1.

9. A pressure sensitive adhesive tape according to claim 8 wherein the flexible support is an impregnated glass cloth, a polyester polymer, a polyimide polymer, or a chemically treated fluorocarbon polymer support.

10. A solventless organopolysiloxane composition curable to produce a pressure sensitive adhesive comprising by weight:

(A) from 50 to 75 parts by weight of a toluene soluble, resinous copolymer comprising $R_3SiO_{1/2}$ units and $SiO_{4/2}$ units wherein R is a monovalent hydrocarbon radical having from 1 to 6 carbon atoms, the resinous copolymer comprising from 0.2% to 5.0% by weight, based on the total weight of the copolymer, of hydroxyl radicals, at least 95% of all R groups being an alkyl group, the total number of R radicals that are alkenyl radicals being 0-0.5% of all R radicals, the molar ratio of $R_3SiO_{1/2}$ units to $SiO_{4/2}$ units being from 0.6 to 0.9 inclusive;

(B) an alkenyl-terminated polydiorganosiloxane having the general formula

(I) $R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$

wherein each R^1 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, R^2 is an alkenyl group having from 2 to 10 carbon atoms, "m" and "n" are numbers such that the sum of "m" + "n" is equal to a number in the range of from 1 to 300;

(C) an organohydrogenpolysiloxane compatible with the mixture of (A) and (B) and having the general formula

(II) $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$

wherein each R^3 is independently an alkyl group having from 1 to 10 carbon atoms or an aryl group, "a" and "b" each are numbers such that the sum of "a" + "b" is a number in the range of from 1 to 300, there being at least two silicon bonded hydrogen atoms per molecule of (C), no silicon atom bearing more than one silicon bonded hydrogen atom; the total of (B) and (C) being from 25 to 50 parts by weight; the total of (A), (B), and (C) being 100 parts by weight; the molar ratio of silicon-bonded hydrogen groups in (C) to silicon-bonded alkenyl groups in (B) being in the range of from about 0.8:1 to 1.5:1; with the proviso that the total crosslink density of (B) and (C) is from 0.3 to 5.0%, and with the further proviso that the combined viscosities of (B) and (C) are from 10 to 500 mPa.s (centipoises) at 25 °C; and

(D) a catalytic amount of a hydrosilation catalyst.

Patentansprüche

1. Polyorganosiloxan-Zusammensetzung, die unter Erzeugung eines Haftklebers härtbar ist, umfassend, bezogen auf das Gewicht:

   (A) von 50 bis 75 Gewichtsteile eines Toluol-löslichen, harzartigen Copolymers, umfassend $R_3SiO_{1/2}$-Einheiten und $SiO_{4/2}$-Einheiten, worin R ein einwertiger Kohlenwasserstoffrest mit 1 bis 6 Kohlenstoffatomen ist, das harzartige Copolymer von 0,2 bis 5,0 Gew.-%, bezogen auf das Gesamtgewicht des Copolymers, von Hydroxylresten umfaßt, mindestns 95% aller R-Gruppen eine Alkylgruppe sind, die Gesamtzahl der R-Reste, die Alkenylreste sind, 0 bis 0,5% aller R-Reste beträgt, das molare Verhältnis der $R_3SiO_{1/2}$-Einheiten zu den $SiO_{4/2}$-Einheiten im Bereich von 0,6 bis einschließlich 0,9 liegt;

   (B) ein Alkenyl-Endgruppen aufweisendes Polydiorganosiloxan der allgemeinen Formel

   $R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$ (I)

   worin jedes R^1 unabhängig eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Arylgruppe ist, R^2 eine Alkenylgruppe mit 2 bis 10 Kohlenstoffatomen ist, "m" und "n" derartige Zahlen sind, daß die Summe von "m" + "n" gleich einer Zahl von 1 bis 300 ist;

   (C) ein mit der Mischung von (A) und (B) verträgliches Organohydrogenpolysiloxan der allgemeinen Formel

   $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$ (II)

   worin jedes R^3 unabhängig eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Arylgruppe ist, "a" und "b" jeweils derartige Zahlen sind, daß die Summe von "a" + "b" eine Zahl im Bereich von 1 bis 300 ist, mindestens zwei an Silicium gebundene Wasserstoffatome pro Molekül von (C) vorhanden sind, kein Siliciumatom mehr als ein gebundenes Wasserstoffatom trägt, die Gesamtheit von (B) und (C) im Bereich von 25 bis 50 Gewichtsteilen liegt, die Gesamtheit von (A), (B) und (C) 100 Gewichtsteile beträgt, das molare Verhältnis der an Silicium gebundenen Wasserstoffatome in (C) zu den an Silicium gebundenen Alkenylgruppen in (B) im Bereich von 0,8:1 bis 1,5:1 liegt, unter der Bedingung, daß die Gesamtvernetzungsdichte von (B) und (C) im Bereich von 0,3 bis 5,0% liegt und unter der weiteren Bedingung, daß die kombinierten Viskositäten von (B) und (C) im Bereich von 10 bis 500 mPa•s (centipoise) bei 25 °C liegen;

   (D) eine katalytische Menge eines Hydrosilylierungs-Katalysators und

   (E) von 0 bis 10 Gew.-% eines organischen Lösungsmittels.

2. Zusammensetzung nach Anspruch 1, worin die kombinierte Vernetzungsdichte von (B) und (C) im Bereich von 0,3 bis 2,0% liegt und das molare Verhältnis der an Silicium gebundenen Wasserstoffatome in (C) zu den an Silicium gebundenen Alkenylgruppen in (B) etwa 1:1 beträgt.

3. Zusammensetzung nach Anspruch 1, worin der Hydrosilylierungs-Katalysator ein platinhaltiger Hydrosilylierungs-Katalysator ist.

4. Zusammensetzung nach Anspruch 1, orin der platinhaltige Hydrosilylierungs-Katalysator in einer Menge von mindestens 1,0 Gewichtsteil auf 1 Million Teile der Gesamtheit von (A), (B) und (C) vorhanden ist.

5. Zusammensetzung nach Anspruch 1, weiter umfassend einen Inhibitor für den Hydrosilylierungs-Katalysator.

6. Zusammensetzung nach Anspruch 1, worin R, R^1 und R^3 jeweils Methyl sind.

7. Zusammensetzung nach Anspruch 1, worin R^2 eine Vinylgruppe ist.

8. Selbstklebeband, umfassend einen flexiblen Träger, der auf mindestens einer Oberfläche die härtbare Zusammensetzung von Anspruch 1 trägt.

9. Selbstklebeband nach Anspruch 8, worin der flexible Träger ein imprägnierter Glasgewebe-, ein Polyesterpolymer-, ein Polyimidpolymer- oder ein chemisch behandelter Fluorkohlenstoffpolymer-Träger ist.

10. Lösungsmittelfreie Polyorganosiloxan-Zusammensetzung, die zu einem Haftkleber härtbar ist, umfassend, bezogen auf das Gewicht:
(A) von 50 bis 75 Gewichtsteile eines Toluol-löslichen, harzartigen Copolymers, umfassend $R_3SiO_{1/2}$-Einheiten und $SiO_{4/2}$-Einheiten, worin R ein einwertiger Kohlenwasserstoffrest mit 1 bis 6 Kohlenstoffatomen ist, das harzartige Copolymer von 0,2 bis 5,0 Gew.-%, bezogen auf das Gesamtgewicht des Copolymers, von Hydroxylresten umfaßt, mindestns 95% alle, R-Gruppen eine Alkylgruppe sind, die Gesamtzahl der R-Reste, die Alkenylreste sind, 0 bis 0,5% aller R-Reste beträgt, das molare Verhältnis der $R_3SiO_{1/2}$-Einheiten zu den $SiO_{4/2}$-Einheiten im Bereich von 0,6 bis einschließlich 0,9 liegt;
(B) ein Alkenyl-Endgruppen aufweisendes Polydiorganosiloxan der allgemeinen Formel

$$R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2 \qquad (I)$$

worin jedes R^1 unabhängig eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Arylgruppe ist, R^2 eine Alkenylgruppe mit 2 bis 10 Kohlenstoffatomen ist, "m" und "n" derartige Zahlen sind, daß die Summe von "m" + "n" gleich einer Zahl von 1 bis 300 ist;
(C) ein mit der Mischung von (A) und (B) verträgliches Organohydrogenpolysiloxan der allgemeinen Formel

$$R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2 \qquad (II)$$

worin jedes R^3 unabhängig eine Alkylgruppe mit 1 bis 10 Kohlenstoffatomen oder eine Arylgruppe ist, "a" und "b" jeweils derartige Zahlen sind, daß die Summe von "a" + "b" eine Zahl im Bereich von 1 bis 300 ist, mindestens zwei an Silicium gebundene Wasserstoffatome pro Molekül von (C) vorhanden sind, kein Siliciumatom mehr als ein gebundenes Wasserstoffatom trägt, die Gesamtheit von (B) und (C) im Bereich von 25 bis 50 Gewichtsteilen liegt, die Gesamtheit von (A), (B) und (C) 100 Gewichtsteile beträgt, das molare Verhältnis der an Silicium gebundenen Wasserstoffatome in (C) zu den an Silicium gebundenen Alkenylgruppen in (B) im Bereich von 0,8:1 bis 1,5:1 liegt, unter der Bedingung, daß die Gesamtvernetzungsdichte von (B) und (C) im Bereich von 0,3 bis 5,0% liegt und unter der weiteren Bedingung, daß die kombinierten Viskositäten von (B) und (C) im Bereich von 10 bis 500 mPa•s (centipoise) bei 25 °C liegen und
(D) eine katalytische Menge eines Hydrosilylierungs-Katalysators.

Revendications

1. Composition à base d'organopolysiloxane, durcissable et produisant par durcissement un adhésif sensible à la pression, comprenant, en poids:
(A) de 50 à 75 parties en poids d'un copolymère résineux, soluble dans le toluène, comprenant des motifs $R_3SiO_{1/2}$ et des motifs $SiO_{4/2}$, R représentant un groupe hydrocarboné monovalent, ayant de 1 à 6 atomes de carbone, ledit copolymère résineux comprenant de 0,2% à 5,0% en poids, par rapport au poids total du copolymère, de groupes hydroxyle, au moins 95% de tous les groupes R

étant des groupes alkyle et le nombre total de groupes R qui sont des groupes alcényle représentant 0 à 0,5% de tous les groupes R, et le rapport molaire des motifs $R_3SiO_{1/2}$ aux motifs $SiO_{4/2}$ étant de 0,6 à 0,9, bornes incluses,

(B) un polydiorganosiloxane à terminaisons alcényle, répondant à la formule générale:

(I) $R^2R^1{}_2SiO(R^1{}_2SiO)_m(R^2R^1SiO)_nSiR^1{}_2R^2$

dans laquelle chaque R^1 représente indépendamment un groupe alkyle ayant de 1 à 10 atomes de carbone ou un groupe aryle, R^2 représente un groupe alcényle ayant de 2 à 10 atomes de carbone, m et n sont des nombres tels que la somme m + n est égale à un nombre compris dans l'intervalle allant de 1 à 300,

(C) un organohydrogénopolysiloxane compatible avec le mélange de (A) et (B), répondant à la formule générale:

(II) $R^3{}_2HSiO(R^3HSiO)_a(R^3{}_2SiO)_bSiHR^3{}_2$

dans laquelle chaque R^3 représente indépendamment un groupe alkyle ayant de 1 à 10 atomes de carbone ou un groupe aryle, et a et b sont des nombres tels que la somme a + b est un nombre compris dans l'intervalle allant de 1 à 300, au moins deux atomes d'hydrogène liés à du silicium étant présents par molécule de (C) et aucun atome de silicium portant plus d'un atome d'hydrogène lié à lui,

le total de (B) et (C) représentant de 25 à 50 parties en poids et le total de (A), (B) et (C) représentant 100 parties en poids, le rapport molaire des atomes d'hydrogène liés à du silicium de (C) aux groupes alcényle liés à du silicium de (B) étant compris dans l'intervalle allant de 0,8:1 à 1,5:1, étant entendu que la densité de réticulation totale de (B) et (C) est de 0,3 à 5,0%, et étant entendu que les viscosités combinées de (B) et (C) sont de 10 à 500 mPa.s (centipoises) à 25 °C,

(D) une quantité catalytique d'un catalyseur d'hydrosilation, et

(E) de 0 à 10% en poids d'un solvant organique.

2. Composition selon la revendication 1, pour laquelle la densité de réticulation globale de (B) et (C) est de 0,3 à 2,0% et le rapport molaire des atomes d'hydrogène liés à du silicium de (C) aux groupes alcényle liés à du silicium de (B) est d'environ 1:1.

3. Composition selon la revendication 1, dans laquelle le catalyseur d'hydrosilation est un catalyseur d'hydrosilation renfermant du platine.

4. Composition selon la revendication 1, dans laquelle le catalyseur d'hydrosilation renfermant du platine est présent à raison d'au moins 1,0 partie en poids pour un million de parties du total de (A), (B) et (C).

5. Composition selon la revendication 1, comprenant en outre un inhibiteur pour le catalyseur d'hydrosilation.

6. Composition selon la revendication 1, pour laquelle R, R^1 et R^3 représentent chacun un groupe méthyle.

7. Composition selon la revendication 1, pour laquelle R^2 représente un groupe vinyle.

8. Ruban adhésif sensible à la pression, comprenant un support flexible qui porte sur au moins l'une de ses surfaces, la composition durcissable selon la revendication 1.

9. Ruban adhésif sensible à la pression, selon la revendication 8, pour lequel le support flexible est un support constitué d'une étoffe de verre imprégnée, d'un polymère polyester, d'un polymère polyimide ou d'un polymère fluorocarboné traité chimiquement.

10. Composition à base d'organopolysiloxane, sans solvant, durcissable et produisant par durcissement un adhésif sensible à la pression, comprenant, en poids:

(A) de 50 à 75 parties en poids d'un copolymère résineux, soluble dans le toluène, comprenant des motifs $R_3SiO_{1/2}$ et des motifs $SiO_{4/2}$, R représentant un groupe hydrocarboné monovalent, ayant de 1

à 6 atomes de carbone, ledit copolymère résineux comprenant de 0,2% à 5,0% en poids, par rapport au poids total du copolymère, de groupes hydroxyle, au moins 95% de tous les groupes R étant des groupes alkyle et le nombre total de groupes R qui sont des groupes alcényle représentant 0 à 0,5% de tous les groupes R, et le rapport molaire des motifs $R_3SiO_{1/2}$ aux motifs $SiO_{4/2}$ étant de 0,6 à 0,9, bornes incluses,
(B) un polydiorganosiloxane à terminaisons alcényle, répondant à la formule générale:

(I) $R^2R^1_2SiO(R^1_2SiO)_m(R^2R^1SiO)_nSiR^1_2R^2$

dans laquelle chaque R^1 représente indépendamment un groupe alkyle ayant de 1 à 10 atomes de carbone ou un groupe aryle, R^2 représente un groupe alcényle ayant de 2 à 10 atomes de carbone, m et n sont des nombres tels que la somme m + n est égale à un nombre compris dans l'intervalle allant de 1 à 300,
(C) un organohydrogénopolysiloxane compatible avec le mélange de (A) et (B), répondant à la formule générale:

(II) $R^3_2HSiO(R^3HSiO)_a(R^3_2SiO)_bSiHR^3_2$

dans laquelle chaque R^3 représente indépendamment un groupe alkyle ayant de 1 à 10 atomes de carbone ou un groupe aryle, et a et b sont des nombres tels que la somme a + b est un nombre compris dans l'intervalle allant de 1 à 300, au moins deux atomes d'hydrogène liés à du silicium étant présents par molécule de (C) et aucun atome de silicium portant plus d'un atome d'hydrogène lié à lui,

le total de (B) et (C) représentant de 25 à 50 parties en poids et le total de (A), (B) et (C) représentant 100 parties en poids, le rapport molaire des atomes d'hydrogène liés à du silicium de (C) aux groupes alcényle liés à du silicium de (B) étant compris dans l'intervalle allant de 0,8:1 à 1,5:1, étant entendu que la densité de réticulation totale de (B) et (C) est de 0,3 à 5,0%, et étant entendu que les viscosités combinées de (B) et (C) sont de 10 à 500 mPa.s (centipoises) à 25 °C, et
(D) une quantité catalytique d'un catalyseur d'hydrosilation.